

Effects of electrolyte stratification on performances of AGM valve-regulated lead-acid batteries

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Abstract

Two absorptive glass mat (AGM) valve-regulated lead-acid batteries with concentration and saturation stratification were simulated. Results indicate that the concentration stratification makes the active mass (AM) in lower part discharge deeply, which results in more irreversible sulphate on the negative plate because of inefficient recharge. In saturation stratification, more AM is also discharged in lower part, but the high oxygen recombination and undercharge in the upper part of the negative plate also leads to its sulphation. When the battery is in short-time rest state, the self-charge process occurs in the upper part and self-discharge process in the lower part of the same plate, but the processes differs with rest continuing. All these make the negative plate sulphation.

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Keywords: Electrolyte stratification; Oxygen recombination; Sulphation; Utilization of active material; Valve-regulated lead-acid batteries

1. Introduction

For the gradual exhaust of the fossil resources and the increasing rise in the price of petroleum, more attentions are paid to the power sources with high specific energy. Regretfully, most of them are in trial or only suitable for limited application because of immature technique or exorbitant cost [1–7]. Owing to many advantages, valve-regulated lead-acid (VRLA) batteries become the most economical and best near-term electrochemical storage system and serve in many fields [8], especially prevalent in cycling applications [9–11]. However, there are still some deficiencies under improvement [12–14].

Electrolyte stratification is one of the common failure modes in flooded lead-acid batteries [15]. During discharging, water is produced from the plates and moves upwards because it is lighter than the surrounding electrolyte. During recharging, sulphuric acid is liberated from the plates and moves downwards as it is heavier than bulk solution. Thus, the electrolyte in the lower part of a cell tends to be more concentrated than that in the upper part [16–18], especially during discharging [19]. The development of vertical concentration gradient will baffle uni-

form utilization of active mass (AM), and result in irreversible formation of PbSO_4 , consequently shorten the service life of the cell [20]. Electrolyte stratification can be overcome through agitation of the electrolyte by vigorous gassing during extended overcharging periodically.

Many workers have discussed electrolyte stratification. Alavyoon and his colleagues proposed a two-dimensional mathematical model to study free convection and stratification of electrolyte, and they measured the concentration and velocity profiles using holographic laser interferometry (HLI) and laser Doppler velocimetry (LDV), respectively. The experimental results agree well with the theoretical predication [21,22]. Mattera found that in PV applications, electrolyte stratification occurs often and it favors irreversible sulphation, subsequently resulting in premature capacity loss. This degradation was confirmed by using radioelement detection [23].

In AGM VRLA batteries, the immobilization of electrolyte reduces the degree of electrolyte stratification, but at the same time, it also removes its possible remedy because violent gassing is impossible. So electrolyte stratification is a common phenomenon in the large and aged AGM VRLA cells and batteries [24–26]: (i) the gravity action leads to the development of concentration gradients in the liquid phase; (ii) the taller separator increases the resistance of electrolyte flow vertically, and the water loss reduces the electrolyte, so the saturation of the separa-

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tor and plates in the upper part decreases [27]. However, there are little open data discussed on stratification in AGM VRLA batteries. In this work, the electrolyte stratification in AGM VRLA battery is simulated in two aspects of concentration and saturation of electrolyte, it is expected to investigate the kinetics of electrolyte stratification and its impact on the performances.

2. Experimental

The simulation of the electrolyte stratification was conducted as cutting a tall cell, in which the electrolyte stratification has occurred, into two parts in vertical direction. The concentration and saturation of electrolyte in two cells are controlled to match those of the real upper and lower part in a single cell.

2.1. Cell preparation

Four identical AGM VRLA cells were prepared; each of them consisted of seven positive and eight negative plates. The C_2 capacity of each cell was 10 Ah. The four cells were divided into two groups:

- *The first group:* the electrolyte with 1.30 and 1.34 sp. gr. H_2SO_4 were filled into two cells, representing the upper and lower parts in the large AGM cell with concentration stratification, respectively. The electrolyte was just absorbed in AGM, but no redundancy. It was resumed as 100% saturation.
- *The second group:* the same H_2SO_4 concentration (1.32 sp. gr.) was filled into another two cells, but the amount was different: one was the same as the first group, regarded as 100% saturation; the other amount was only 93%, i.e., 93% saturation.

2.2. Cell test

The measurement circuit was shown in Fig. 1. The two paralleled cells were used to simulate the upper and lower part in a single stratified cell. The two identical standard resistances, R_1 and R_2 (75 mV/30 A), were introduced to measure the current of each paralleled cell. It is the number of dividing R_1 or R_2 by the voltage of R_1 or R_2 recorded by Acquisition/Switch Unit.

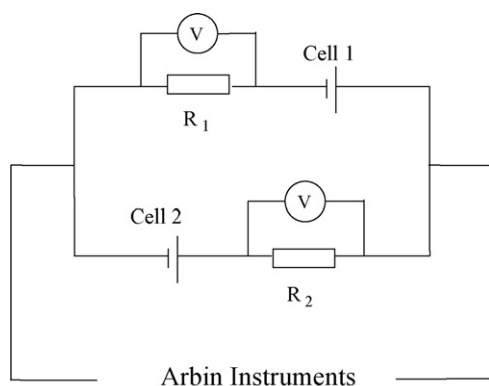


Fig. 1. The test circuit of the simulated cells with electrolyte stratification.

The paralleled circuit firstly charged at the current-limited constant-voltage (IU) with 5 A, 2.5 V, then at 1 A for 1 h. The total charging time was limited within 7 h. The discharge current was 10 A till each cell voltage dropped to 1.75 V. The charge and discharge processes were conducted by Arbin Instruments BT 2000, and the data were acquired by HP 34970A data Acquisition/Switch Unit connected to PC. The electrode potential reported was against the Hg/Hg₂SO₄/H₂SO₄ (1.320 sp. gr.) reference electrode. The appearance was observed by the scanning electron microscopy (SEM) (JSM-35CF).

3. Results and discussion

In large AGM VRLA batteries, acid drainage and electrolyte stratification often occur, especially accelerated by deep-discharge cycles [28]. The lower part has concentrated electrolyte because of the gravity action, and the wicking rate of electrolyte to the upper part becomes difficult, so the saturation in the upper part is lower than that in the lower part. Above two effects are named as concentration stratification and saturation stratification, respectively.

3.1. Concentration stratification

Fig. 2A shows the changes of the discharge current of two cells with different concentration in the 75th cycle. It indicates that the cell with more concentrated acid, equivalent to the lower part in a large AGM cell, has higher discharge current than that with less concentrated acid, which is equivalent to the upper part of a cell. And the current difference is about 1.4 times at the beginning of discharging. Then, the difference decreases grad-

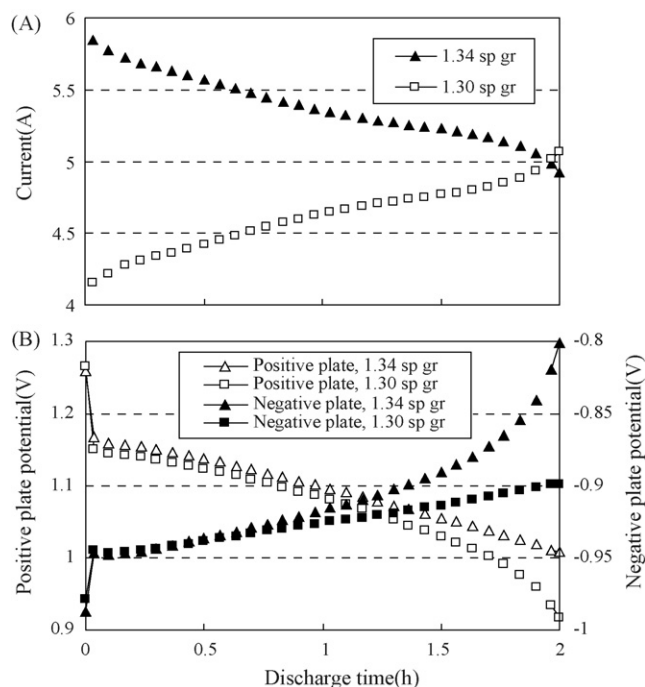


Fig. 2. The changes of (A) discharge current and (B) electrode potential in the 75th cycle in concentration stratification.

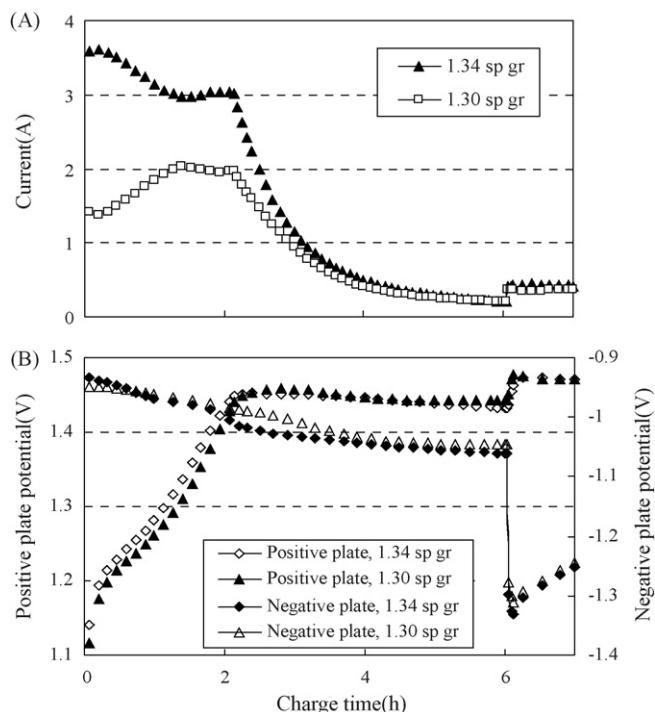


Fig. 3. The changes of (A) charge current and (B) electrode potential in the 75th cycle in concentration stratification.

ually. Near the end of discharge, two currents get equal. After that, the upper part discharges at a higher rate than the lower part instead.

The changes of the corresponding electrode potential during the 75th discharging cycle are given in Fig. 2B. It indicates that at the initial discharge in the lower part, the positive plate potential is more positive and the negative plate potential is more negative. That is to say, the voltage of the lower part is higher than that of the upper part, as favors the discharge in the lower part, and its AM utilization is prior to that in the upper part. During the latter discharging, the negative electrode potential in the upper part with less concentrated acid decreases more quickly than that in the lower part. The reason is that the higher discharge rate in earlier period makes more and finer PbSO_4 crystals formed in the negative electrode in the lower part, thus the negative plate passivates easily and the AM utilization decreases. So the upper part discharges more near the end of stage.

Fig. 3 shows the changes of the charge current and electrode potential followed after the 75th discharging. It can be seen from Fig. 3A that at the beginning of charging, the current in the lower part with more concentrated acid is about 2.7 times higher than that in the upper part. Then, the current difference decreases gradually. After 2.1 h, the cell voltages are limited at 2.5 V, and the current in the lower part is still about 1.5 times higher than the upper cell because the SOC of the former is still lower. So the charge current in the lower part is always relatively high. In Fig. 3B, the positive electrode in the upper part and the negative electrode in the lower part do not charge more although they discharged more. Obviously, these two electrodes charge insufficiently because of the formation of irreversible sulphate. In the last period of constant-current, both two nega-

tive plate potentials shift to positive because of oxygen recombination.

3.2. Saturation stratification

The prepared two cells with 100% and 93% separator saturation of the second group were connected as Fig. 1, representing the lower and upper part in an AGM VRLA cell with saturation stratification, respectively.

Fig. 4 shows the evolution of the discharge current and electrode potential in the 75th cycle. It indicates that at the beginning of discharging, shown in Fig. 4A, the cell with high saturation, which is equivalent to the lower part of a cell, discharges more than the cell with low saturation, equivalent to the upper part of a cell. However, the current difference is less than that in Fig. 2A. Two currents get the same at about 1.8 h, then the upper part charges more than the lower part, and the current difference between two cells enlarges increasingly. It is obvious that the lower part discharges importantly in the most of period, and its AM utilization is high. So there are much more PbSO_4 particles formed in this part, thus the ionic diffusion and conductivity between AM decrease. As can be seen from Fig. 4B, the negative electrode potential in the upper part is more positive than that in the lower part during total discharging. The reason is that, when the separator saturation is low, the metal lead above electrolyte can easily react with the surplus oxygen in the space house, and shift more positive.

The changes of charge current and electrode potentials in the 75th cycle are shown in Fig. 5. The lower part with high saturation charges at a little higher current because it discharges

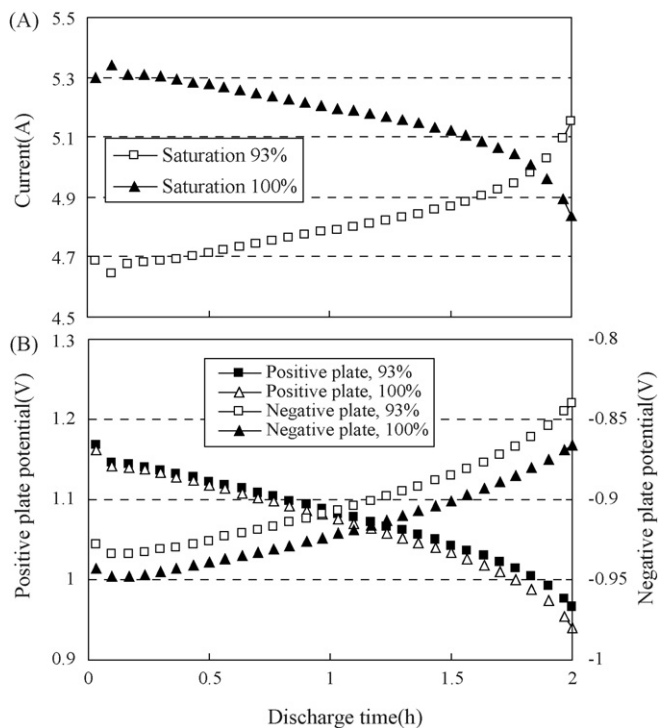


Fig. 4. The changes of (A) discharge current and (B) electrode potential in the 75th cycle in saturation stratification.

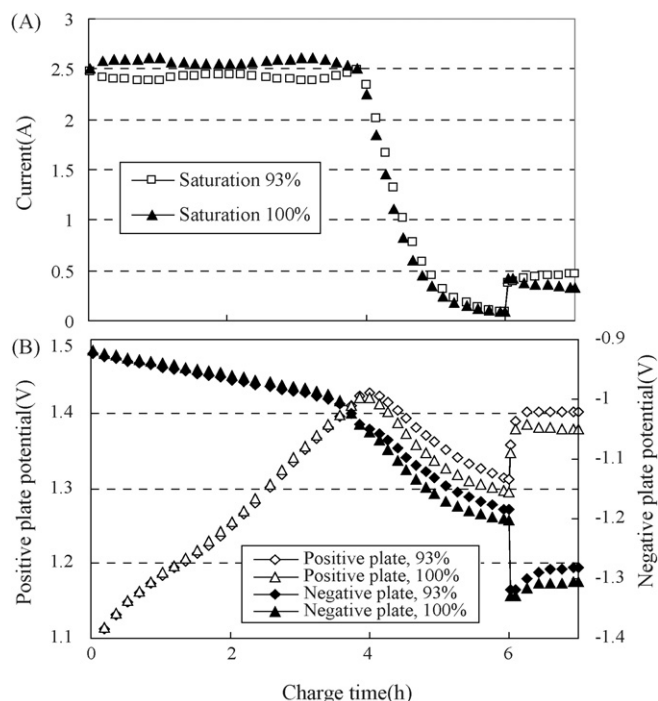


Fig. 5. The changes of (A) charge current and (B) electrode potential in the 75th cycle in saturation stratification.

more, and there are many PbSO_4 particles can be transformed to SO_4^{2-} . At the end of constant-current (about 4 h), the two currents come to the same value. Contrast to the higher current difference in Fig. 3A, the lower part in saturation stratification charges efficiently than that in concentration stratification. In the period of the third charge (6 h till the end), the current in the upper part is higher because the rate of oxygen recombination is higher than that in the lower part, and partial current is consumed by oxygen evolution [29]. This can be seen from the electrode potential changes in Fig. 5B, in the period of limited-voltage charging, the negative electrode potential in the upper part is much positive, correspondingly, its positive potential shifts more positive than that in the lower part. Another evidence of oxygen recombination is that the exterior of the cell with low saturation feels hotter, it is clear that the higher rate of oxygen recombination releases more heat. Evidently, the upper part is difficult to get full-charged.

3.3. Comparison of two kinds of stratification

As discussed previously, the lower part discharges more than the upper part, whether in concentration stratification or saturation stratification. But the lower part does not always charge much more. So the sulphation in the lower part is serious. However, the upper part in saturation stratification always under-charges because of oxygen recombination, so there is many sulphates also exist in this part.

Fig. 6 shows the changes of discharge current in the 75th and 125th cycles. In concentration saturation (Fig. 6A), the discharge time shortens, and the current difference increases at the beginning of discharging with cycles increased. It is obvious

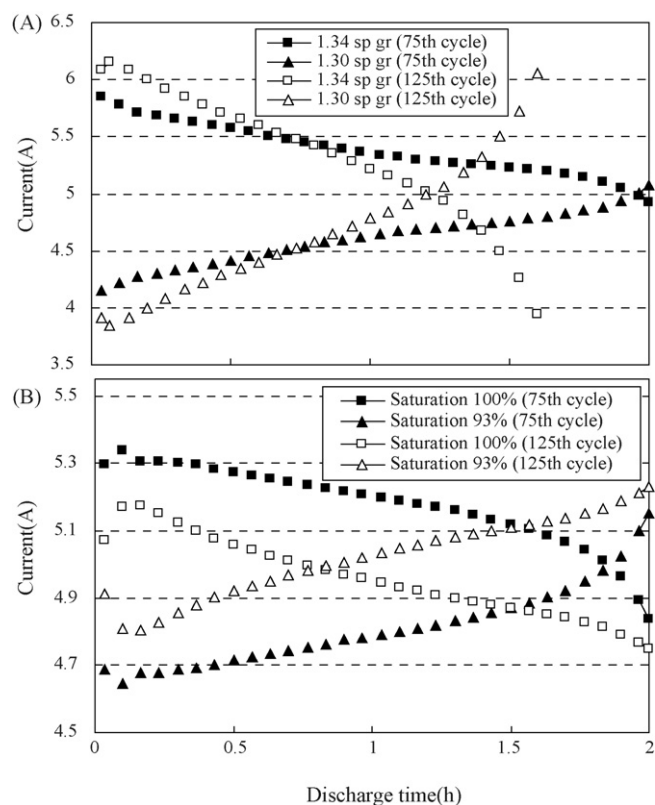


Fig. 6. The changes of discharge current in the 75th and 125th cycles in (A) concentration and (B) saturation stratification.

that the concentration difference between the upper and lower part becomes more. The lower part has more concentrated acid for loss water, and it discharges more than before. In saturation stratification, however, the discharge time differs few, and the current difference reduces with cycles increased. It indicates that the saturation difference of the two simulated cells is less than before. And that, because of the formation of irreversible sulphate both in the upper and lower part, the AM utilization declines and the current decreases.

Fig. 7 shows the evolution of total discharge capacity of the paralleled simulated cells with concentration and saturation

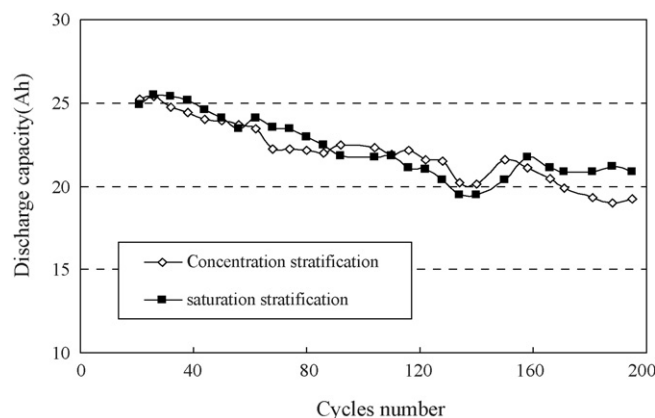


Fig. 7. Evolution of total discharge capacity of the simulated cells with concentration and saturation stratification within 200 cycles.

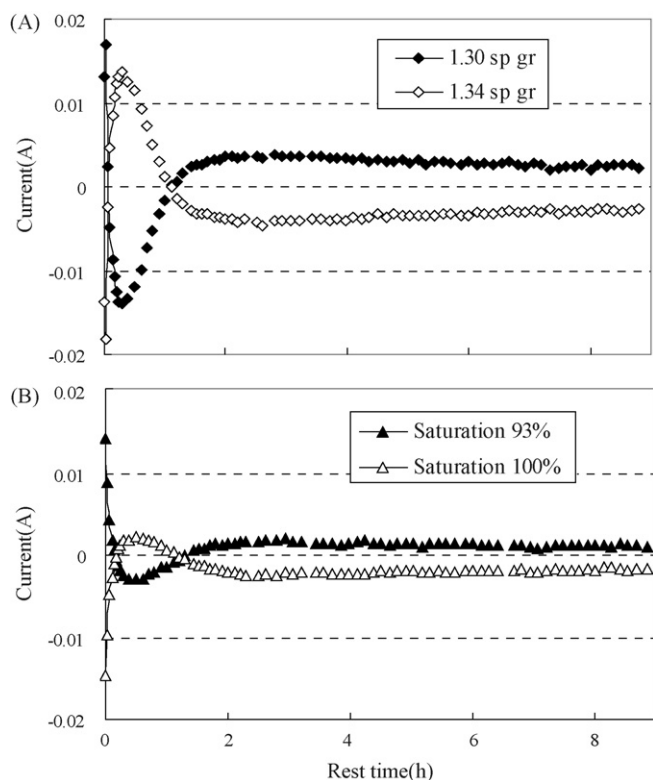


Fig. 8. Evolution of the current in the upper and lower part of the fully charged cells with (A) concentration and (B) saturation stratification in the rest stage.

stratification within 200 cycles. It indicates that the capacity loss is significant in the former 130 cycles. Obviously, the electrolyte stratification becomes worse gradually, and the irreversible sulphation makes the AM less, thus the cell discharges less.

When the tests are terminated, two groups full-charged cells are left rest in paralleled, the current changes recorded are shown in Fig. 8. It can be seen that, in both concentration and saturation stratification, the lower and upper parts are unbalanced, and the local charge and discharge simultaneously occur on the same plate. At the beginning of relaxation, the upper part discharges while the lower part recharges. This is different with that in flooded battery [23], it is resulted by the oxygen recombination in the AGM battery. There is a small quantity of oxygen left in the gas space, and they react with NAM and transformed to PbSO_4 , so the upper part discharges. Till the oxygen is used up, the lower part discharges while the upper part is charged because of more concentration and/or higher saturation, discussed as in Sections 1 and 2. Then the current maintains a relative fixed value till the end. It can be seen that when the charged AGM battery is left unused chronically, the upper part is recharged and the lower part is more deeply discharged.

The internal resistance (IR) of individual cell is measured by applying a short current pulse with 5 A within 1 ms and measuring the response of the voltage. The IR of the cell is thus determined and is shown in Table 1. Clearly, the measurement includes all polarization resistance. It indicates that the lower part has a relative higher resistance than the upper part in concentration stratification. At saturation stratification, the IR differs

Table 1

The internal resistance of charged cells after test

Internal resistance (m Ω)	
Concentration stratification (g cm $^{-3}$)	
1.34	8.05
1.30	7.41
Saturation stratification (%)	
100	7.11
93	7.13

little. Evidently, the higher resistance of cell is caused by the formation of inactive lead sulphate.

To further conform the results, the appearances of the charged NAM are observed by SEM. Fig. 9 is the SEM in concentration stratification; it indicates that NAM in two parts has lost initial dendritic lead structure. There are much more sand-like, poorly crystallized PbSO_4 particles composed in NAM of the lower part. Fig. 10 shows that there are more and larger PbSO_4 formed in the SEM of the upper part in saturation stratification. It is resulted from the higher oxygen recombination, which leads to the upper part under-charged, thus to irreversible sulphation.

The two group cells are performed post-mortem analyses. It is found that large-scale softening and shedding occurred in the positive plates. In the lower part in concentration stratification, the high concentration leads to the oxidation of grids and speeds up the aging of AM, thus results in the positive plates relax and softening seriously. In the upper part in saturation stratification, the oxygen reduction makes the negative potential shift

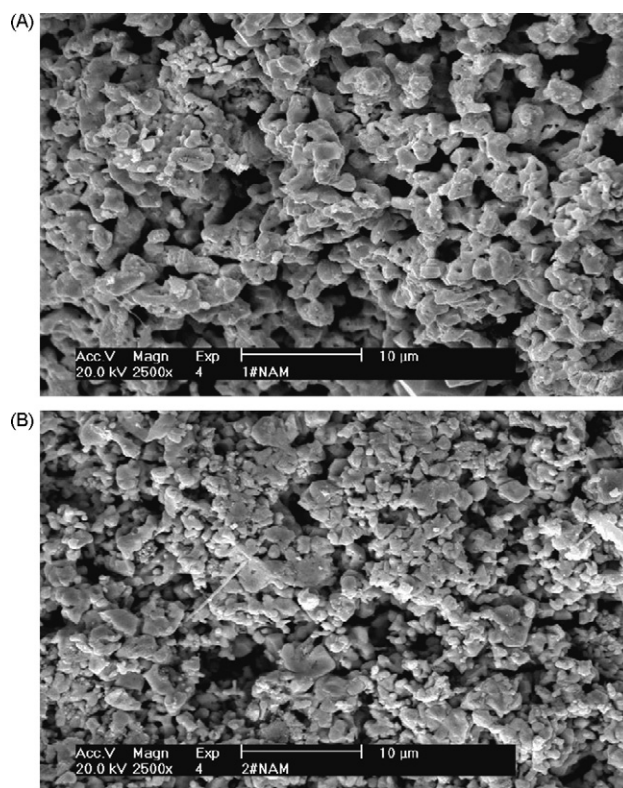


Fig. 9. SEM of the fully charged NAM in simulated cells with concentration stratification. (A) 1.30 and (B) 1.34 sp. gr. H_2SO_4 .

Table 2
The chemical amount in charged plates after test

	Concentration stratification		Saturation stratification	
	The upper part	The lower part	The upper part	The lower part
PbSO ₄ content of negative plate (%)	18.6	25.5	21.4	18.4
PbO ₂ content of positive plate (%)	81.1	85.2	84.2	87.3

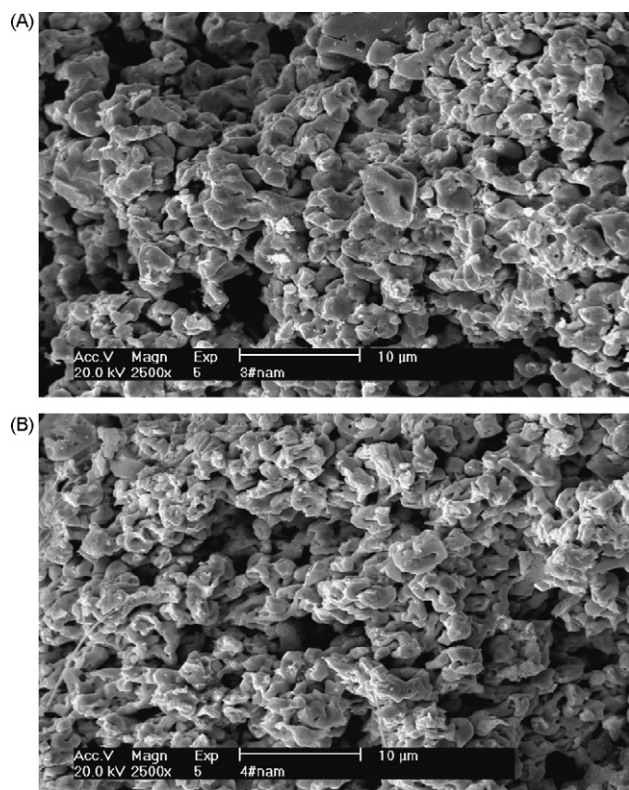


Fig. 10. SEM of the fully charged NAM in simulated cells with saturation stratification. (A) 93% and (B) 100% saturation.

positively, thus the positive potential shifts more positive correspondingly at limited-voltage charging. This accelerates the corrosion of the positive grids, which expands and results in poor conductivity between the grid and AM, and arises more softening and shedding.

To evaluate the consumption of lead dioxide and the formation of lead sulphate, the AM is analyzed. The results are established in Table 2. It can be seen that there are more PbSO₄ formed on the negative plates in the lower part with more concentration and the upper part with lower saturation. The unreacted PbO₂ on positive plates in the lower part with more concentrated acid is more than that in the upper part because the upper positive plate charges ineffectively (as shown in Figs. 2 and 3). In the upper part in low saturation, the irreversible sulphation is higher than that in the lower part for the high rate of oxygen evolution.

4. Conclusions

In the study on the electrochemical behavior of the two paralleled cells with different electrolyte, it is obvious that electrolyte

concentration and/or separator saturation exerts much influence on the performance of the cells. The higher electrolyte concentration and/or higher separator saturation makes AM utilization increase so that the cell discharges more. On the other hand, the frequent undercharge leads to the formation of sulphation and reduce of the discharge performance. In the cell with lower saturation, there are also many irreversible PbSO₄ crystals because of the high rate of oxygen recombination.

Practically, the measurement circuit in this paper are the same as the condition in a large cell. So the two paralleled cells can be looked upon as the simulation of the lower and upper part in a real AGM VRLA cell in which electrolyte stratification have occurred. The results indicate that concentration stratification in the electrolyte results in the un-uniform utilization of AM. At the earlier period of discharge, the AM utilization in the lower part is prior to that in the upper part, so the lower part discharges at a higher current. This makes more and finer PbSO₄ crystals formed in the negative electrode in the lower part. The irreversible sulphation occurs easily because the cell charges insufficiently, resulting in the negative plate to be passivated and the AM utilization decreases. So the upper part discharges more near the end of discharging.

In the upper part, however, the saturation is low and the rate of oxygen recombination is high. The PbSO₄ formed on the positive plates during discharging cannot be oxidized entirely into AM because partial current consumes in oxygen evolution. It is difficult to get full-charged, so the irreversible sulphation is serious in the upper part. And that, the contact of AM gets incompact, the IR of plates becomes higher, so the AM utilization becomes more uneven. When the fully charged battery is in relaxation, the self-charge process occurs in the upper part and self-discharge process in the lower part of the same plate within a relatively brief time, but the processes reverses with rest prolonged. The longer the relaxation, the more discharge in the lower part, and the more capacity loss.

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